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Title: Recent progress in catalytic conversions of carbon dioxide

Development of new reactions and catalysts for the chemical fixation of carbon dioxide (CO2) is needed to overcome its kinetic and thermodynamic stability. An overview is presented of organic and metal catalysts with excellent activity and selectivity developed for various chemical conversions of CO2.

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PERSPECTIVE

Recent progress in catalytic conversions of carbon dioxide

Chihiro Maeda,* Yuki Miyazaki and Tadashi Ema*

Chemical fixation of carbon dioxide (CO_2), which is an inexpensive and renewable carbon source, is becoming more and more important. The development of both new reactions and new catalysts is needed to overcome the kinetic and thermodynamic stability of CO_2. Organic and metal catalysts with unique and excellent activity and selectivity have been developed for various chemical conversions of CO_2. In this perspective, we provide an overview of the recent progress in this field, classifying it into several categories, where each research is concisely summarized one by one using a single reaction scheme, a representative catalyst structure, and/or a catalytic cycle.

1. Introduction

Carbon dioxide (CO_2) is the most abundant renewable carbon source in nature. Chemical fixation of CO_2 is therefore one of the most important subjects in organic synthesis, and much effort has been devoted to this particular subject.[1] Various methods for CO_2 fixation have been developed despite the low reactivity and narrow synthetic scope of CO_2. Although the Kolbe–Schmitt reaction and carboxylation reactions using Grignard reagents are well-known chemical fixations of CO_2,

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these non-catalytic reactions have some limitations. On the other hand, catalytic reactions are considered to be essential for widening and deepening the synthetic utility of CO_2. Both reactions and catalysts need to be developed for this purpose. A large number of inorganic, organic, and metal catalysts have been developed for various chemical conversions of CO_2. The achievements over the past five years are particularly noteworthy. The synthesis of cyclic carbonates or polycarbonates from CO_2 and epoxides, carboxylation reactions with CO_2, reduction of CO_2, and other fascinating reactions have been developed and studied extensively and intensively (Fig. 1). In this perspective, we highlight the latest progress in this field, classifying it into several categories. Each research is summarized concisely using a single reaction scheme and/or a representative catalyst structure even if several derivatives of

Chihiro Maeda

Chihiro Maeda was born in Kanagawa, Japan in 1983. He received his bachelor's degree from Kyoto University in 2005, and he obtained his master's degree in 2007 and doctor's degree in 2010 at Kyoto University under the supervision of Professor Atsuhiro Osuka. In 2010, he started his academic career at Keio University as an Assistant Professor. In 2013, he moved to Okayama University to join the Tadashi Ema research group.
His main research topic is the synthesis and application of novel porphyrin derivatives.
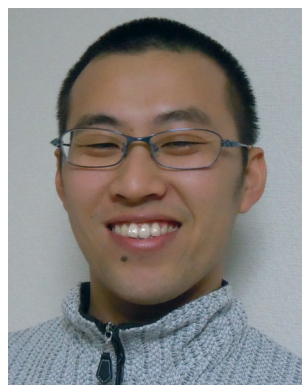
Yuki Miyazaki

Yuki Miyazaki was born in Hyogo, Japan in 1986. He received his bachelor's degree from Okayama University in 2009, and he obtained his master's degree in 2010 and doctor's degree in 2013 at Okayama University under the supervision of Professor Tadashi Ema. His subject during the doctor course was "Metalloporphyrin catalysts for synthesis of cyclic carbonate from CO_2 and epoxide".

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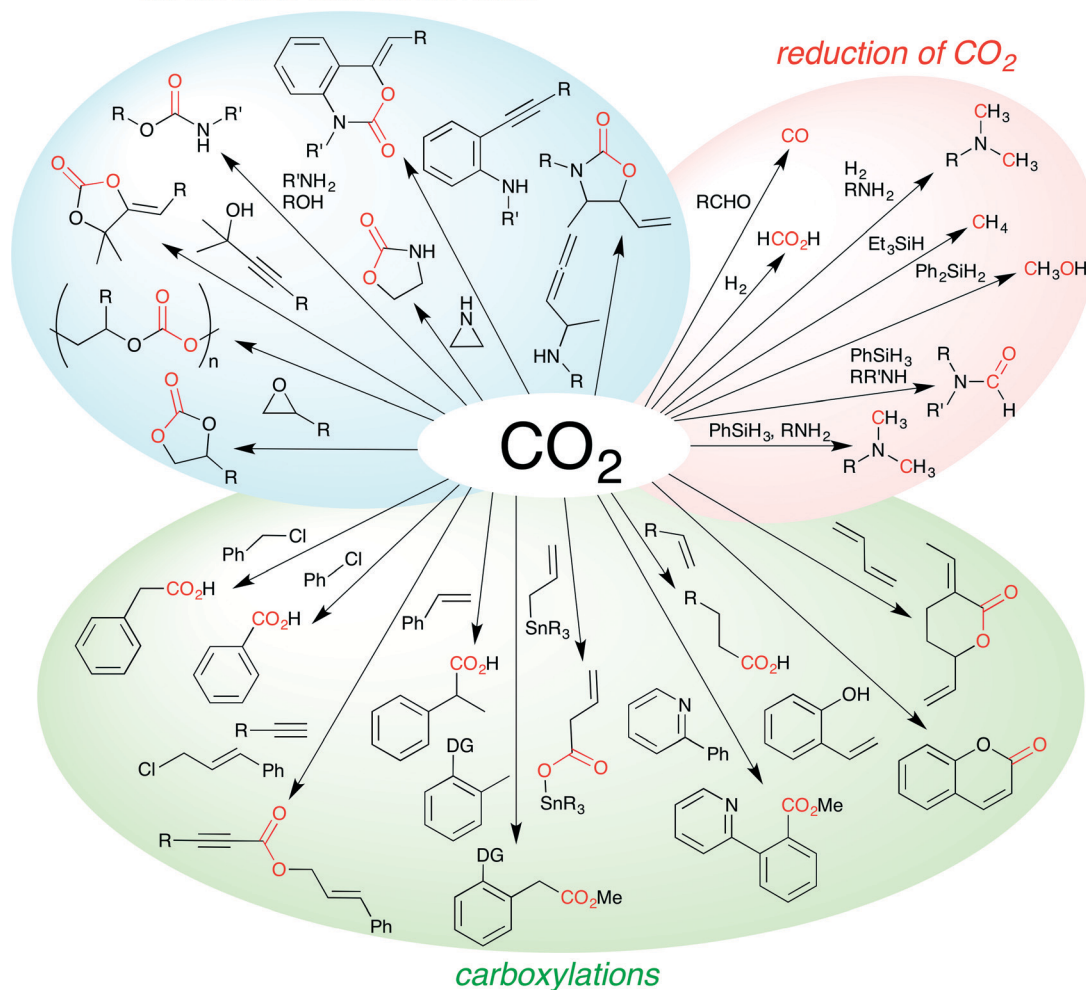This journal is © The Royal Society of Chemistry 2014

Fig. 1 Examples of chemical fixation of CO_2.

substrates and catalysts were reported. In some cases, a catalytic cycle is added to help the readers understand the mechanistic aspect of the reaction and to promote further development of this research field.
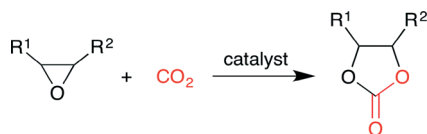
Tadashi Ema was born in Gifu, Japan in 1966. He received his bachelor's degree from Kyoto University in 1989, and he obtained his master's degree in 1991 and doctor's degree in 1994 at Kyoto University under the supervision of Professor Hisanobu Ogoshi. He was appointed as an Assistant Professor at Okayama University in 1994 and was promoted to an Associate Professor in 2002 and a Full Professor in 2012. His research interest is the design and synthesis of unique molecular catalysts.

Tadashi Ema

2. The synthesis of cyclic carbonates from carbon dioxide and epoxides

Cyclic carbonates have been widely used as (i) raw materials for polycarbonates, (ii) electrolytes in lithium-ion secondary batteries, (iii) aprotic polar solvents, and (iv) fuel additives. Although cyclic carbonates have been synthesized by the phosgene method, this method has drawbacks, such as the use of highly toxic gas (phosgene), the formation of hydrogen chloride (byproduct) and the generation of waste water containing dichloromethane (solvent) and salts. Although the phosgene method can produce cyclic carbonates cost-effectively on a large scale, the development of environmentally benign methods is required, such as the catalytic method using CO_2 and epoxides under mild conditions (Scheme 1).

Metalloporphyrin complexes are efficient catalysts (Fig. 2). The Lewis acidic metal center can activate epoxides by coordination. A co-catalyst may be necessary for the nucleophilic ring-opening of the epoxide. Since the pioneering studies by Inoue,[2] several metalloporphyrin complexes such as 1–6, having Al,[2] Cr,[3] Co,[4–6] or Sn[7] as a metal center, have been developed.

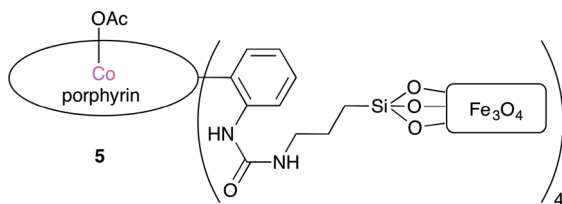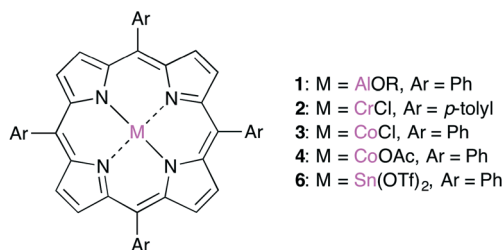**Scheme 1** The synthesis of cyclic carbonates from epoxides and CO_2.

1: M = AlOR, Ar = Ph
2: M = CrCl, Ar = p-tolyl
3: M = CoCl, Ar = Ph
4: M = CoOAc, Ar = Ph
6: M = Sn(OTf)$_2$, Ar = Ph

Fig. 2 Metalloporphyrin catalysts **1–6**.

R = O(CH$_2$)$_6$N+Bu$_3$Br$^-$

Fig. 3 Bifunctional catalyst **7**.

Scheme 2 A plausible catalytic cycle *via* the cooperative activation of epoxide with a bifunctional catalyst.

Recently, Co porphyrin complex **4** was reported by Jing and co-workers.[5] The screening of central metals, axial ligands and co-catalysts indicated that a combination of **4** and phenyltrimethylammonium tribromide (PTAT) showed the highest catalytic activity under mild conditions. The Co porphyrin complex immobilized on magnetic nanoparticles **5** was also developed.[6] This heterogeneous catalyst could be recycled by using a magnet up to 16 times with >90% conversion with a low catalyst loading (0.14 mol%).

Tangestaninejad, Moghadam and co-workers have studied Sn porphyrin complex **6**.[7] The electron-withdrawing axial ligand made the Sn^{IV} center more electron-deficient, which led to a strong coordination of the epoxide and an improvement of the catalytic activity. The quaternary ammonium cation in the co-catalyst was found to be important for the enhancement of the nucleophilicity of the counter anion. The reaction is proposed to be accelerated by the activation of both the epoxide and CO_2 at the Lewis acidic Sn^{IV} center.

More recently, Ema and co-workers reported a highly active bifunctional catalyst **7** (Fig. 3).[8] The Mg center and Br$^-$ ion in **7** acted as a Lewis acid and a nucleophile, respectively. As shown in Scheme 2, this reaction is proposed to be initiated by nucleophilic attack by the Br$^-$ ion on the less hindered side of the epoxide activated by coordination to the Mg center. The oxyanion generated by ring-opening then attacks CO_2 to give a CO_2 adduct. The subsequent cyclization gives the product. The use of 0.0008 mol% of **7** at 120 °C resulted in 83% conversion of the epoxide into cyclic carbonate with a TON of 103 000. The authors also developed an immobilized version of this bifunctional catalyst. Zn porphyrin was immobilized on biogenous iron oxide *via* four quaternary ammonium bromide groups.[9] This organic–inorganic hybrid
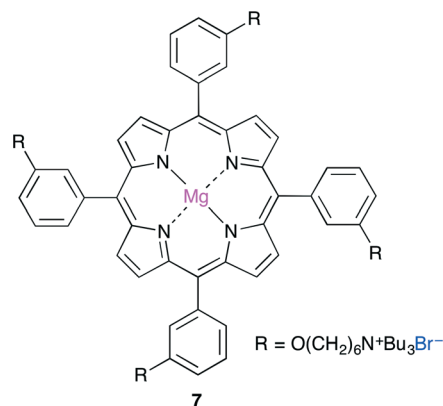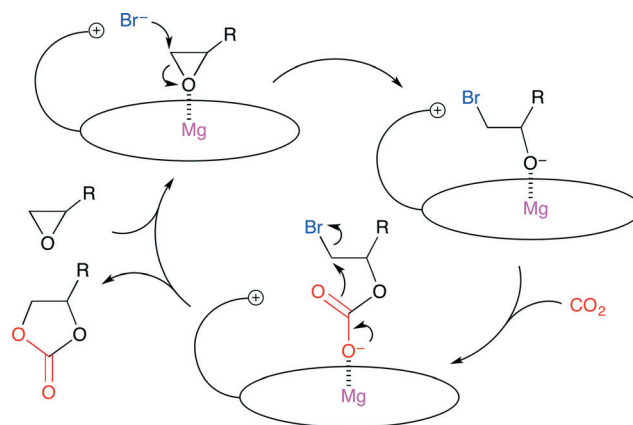
catalyst showed a high activity even after recycling ten times without the loss of catalytic activity.

Ulusoy and co-workers developed a cationic diimine–Ru^{II} complex **8** (Fig. 4).[10] **8** is very attractive due to the easy preparation and chemical stability, and cyclic carbonate could be produced with a low catalyst loading (0.1 mol%). Cyclic voltammetric measurements of several Ru^{II} diimine complexes indicated that **8** had the lowest oxidation potential. This result might be attributed to the electron-donating substituents (NEt$_2$) in **8**.

North and co-workers investigated dimeric Al(salen) complexes (Fig. 5).[11] Bimetallic complex **9** immobilized on the
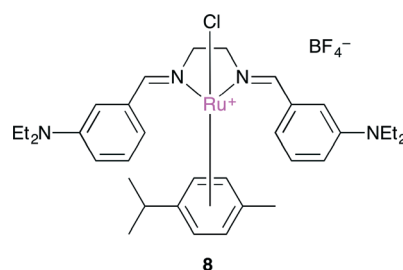

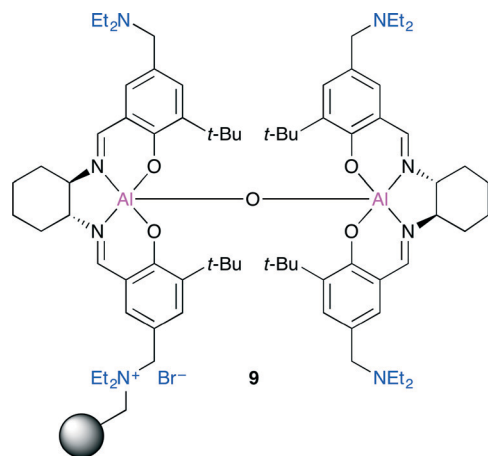**Fig. 4** Cationic diimine–Ru^{II} complex **8**.

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Fig. 5 Immobilized dimeric Al(salen) complex 9.

Scheme 3 The synthesis of Al complex 11.

Merrifield resin *via* an ammonium bromide group showed a high catalytic activity, and 9 was the first heterogeneous catalyst capable of showing catalytic activity at atmospheric pressure of CO_2 at room temperature. The application of 9 to a continuous flow reactor system may be feasible. Although catalyst 9 contains only a single ammonium bromide, 9 showed the highest catalytic activity, which indicated that the amino groups in 9 played an important role in activating CO_2.

Kleij and co-workers reported a trinuclear bifunctional catalyst 10 derived from a tetraoxo bis-Zn(salphen) complex (Fig. 6).[12] The coordinating I^- ion and central Zn atom behave as a nucleophile and a Lewis acid, respectively. The proposed catalytic cycle is as follows. (i) The dissociation of one or two I^- ion occurs. (ii) The epoxide coordinates to the central Zn atom of 10. (iii) The I^- ion attacks the coordinated substrate to form a Zn–alkoxide intermediate. (iv) CO_2 insertion gives a linear carbonate structure. (v) The cyclic carbonate is produced through the ring-closure by the intramolecular nucleophilic attack. In addition, catalyst 10 can be reused up to five times without the loss of catalytic activity.

They also reported an Al complex 11 based on an amino triphenolate ligand (Scheme 3).[13] By using 11 and tetrabutylammonium iodide (TBAI) as a co-catalyst (100 equiv. of 11) at 90 °C, a high TOF (36 000 h^{-1}) and TON (112 000) were achieved. The
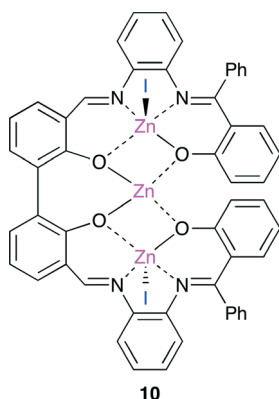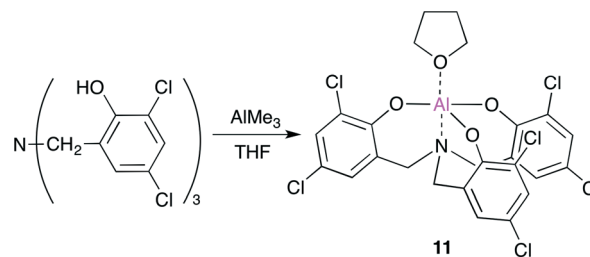
catalytic system also displays a wide substrate scope and functionality tolerance.

Recently, metal–organic frameworks (MOFs) have received much attention from the viewpoint of gas storage, product separation, magnetism and catalysis. Han and co-workers developed a heterogeneous binary catalyst system for cyclic carbonate synthesis.[14] They conducted the reaction using MOF-5 [$Zn_4O(BDC)_3$ (BDC = benzene-1,4-dicarboxylate)] 12 (Fig. 7), which was prepared by the copolymerization of a Zn_4O cluster with BDC, in the presence of tetrabutylammonium bromide. Although most heterogeneous catalysts need a high reaction temperature (>100 °C) and co-solvent, this catalytic system could produce cyclic carbonate in a high yield at atmospheric CO_2 pressure at 50 °C. The effect of the CO_2 pressure on the catalytic activity was investigated. A high catalytic activity was exerted at 1–6 MPa, and the yield of cyclic carbonate decreased with an increase in the pressure from 6 to 12 MPa. This is because propylene oxide was dispersed in CO_2, which decreased the reaction rate.

Ionic liquid 13 with the hydroxy group was developed by Zhang and co-workers (Fig. 8).[15] The catalytic activities of several ionic liquids were compared with quaternary onium salts and urea. 13 showed the highest catalytic activity, selectivity and reusability without any co-catalyst and co-solvent. This is due to the hydrogen bond of the hydroxy group that activates epoxide efficiently. Moreover, investigations on the solvent effect indicated that protic solvents such as water and methanol tended to be more suitable than aprotic solvents such as dimethylcarbonate and DMF.

On the basis of this observation, they postulated that water should be a good medium for the synthesis of cyclic carbonates.[16] A small amount of water was added to the reaction mixture, and various metal halides, ionic liquids and onium salts were screened. As a result, butyltriphenylphosphonium iodide (PPh$_3$BuI) was found to be the most efficient catalyst. The effect of the amount of water was then investigated
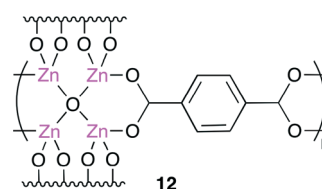

Fig. 6 Trinuclear bifunctional catalyst 10.

Fig. 7 The structure of MOF 12.

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Fig. 8   Ionic liquid 13.

Fig. 10   Hydrogen bonding between the diol and epoxide.

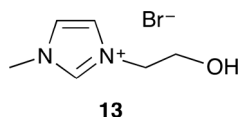Fig. 11   Immobilized ionic liquid 15.

Fig. 12   Ionic liquid 16.

in detail. The addition of 0.33 mol% of water remarkably accelerated the reaction to give a maximal product yield. The TOF value was four-fold higher than that in the absence of water. A further increase in the amount of water decreased the yield and selectivity because of the side reaction giving 1,2-propylene glycol. Other solvents with or without hydroxy groups were also tested. Water was the best solvent for PPh$_3$BuI, suggesting that protic solvents with hydroxy groups are good promoters to improve the catalytic activity of the catalyst.

A binary catalyst system composed of cellulose 14 and KI was reported by Jiang, Han and co-workers (Fig. 9).[17] They envisioned that cellulose, which is abundant in nature, might be able to activate epoxide by the hydrogen bond, and tested cellulose and various alcohols for catalytic activity. The cellulose–KI combination was found to be very active, stable, and recyclable. Based on the results that other 1,2-diols also showed a high catalytic activity, the two adjacent hydroxy groups of cellulose or 1,2-diols seem to activate epoxide *via* double hydrogen bonds (Fig. 10).

Park and co-workers developed a carboxylic acid-functionalized ionic liquid, which was immobilized on silica gel.[18] A series of ionic liquids with or without the carboxyl group and different halide anions were prepared. As a result of screening, 15 showed a high catalytic activity and selectivity (Fig. 11). The immobilized ionic liquids with other functional groups such as the hydroxy group exhibited a lower catalytic activity. The non-functionalized ionic liquid increased the conversion rate but with a lower selectivity in the presence of a small amount of water. In contrast, when a small amount of acetic acid was added to the non-functionalized ionic liquid, the reaction became much faster, yielding a much higher conversion and selectivity. Therefore, the carboxyl group of 15 improved the catalytic performance probably by hydrogen bonding with the epoxide.

He and co-workers developed ionic liquid 16 with strong Lewis basic 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), which could be reused at least five times (Fig. 12).[19] The reaction intermediates were investigated by using *in situ* FT-IR spectroscopy. 16 can activate CO$_2$ and epoxide through carbamic acid formation and the hydrogen bond, respectively. Moreover, 16 could easily convert ethylene carbonate produced from ethylene oxide into dimethyl carbonate by treating with methanol in one pot.
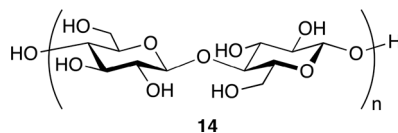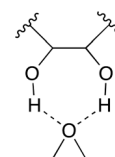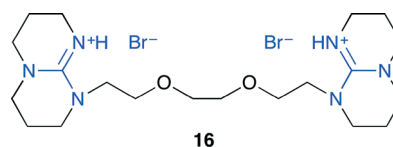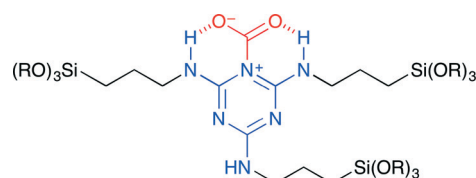
Park and co-workers synthesized periodic mesoporous organosilica (PMO) 17 from N^2,N^4,N^6-tris(3-(triethoxysilyl)propyl)-1,3,5-triazine-2,4,6-triamine (TBTS).[20] This is the first application of the nitrogen-rich PMO to the coupling reaction of CO$_2$ with epoxides. The SEM and TEM measurements revealed that TBTS-PMO had a uniform hexagonal plate morphology with short channels, which were perpendicularly arranged to the platelets. CO$_2$ may be adsorbed at the TBTS-PMO surface to form pseudo-cyclic carbamate (Fig. 13). The cooperative action of the triazine moiety and the amino NH group seems to play an important role in the activation of CO$_2$. DFT calculations supported this proposal.

Sakai and co-workers proposed an ammonium betaine framework for the activation of CO$_2$ to give a reactive intermediate that may be useful for various organic transformations (Fig. 14).[21] The aryloxide anion has both nucleophilic and leaving abilities, both of which are essential features for catalysis, and the quaternary ammonium cation may stabilize the anion formed by the nucleophilic addition to CO$_2$. Among eight candidates, 18 was found to be the most active. A metal-free, halogen-free and solvent-free organocatalytic reaction was achieved with 1 mol% catalyst loading.

Lu and co-workers reported the N-heterocyclic carbene (NHC)-immobilized MCM-41 catalyst 19 (Fig. 15).[22] It is well

Fig. 9   The structure of cellulose.

Fig. 13   A proposed mode of CO$_2$ activation of 17.

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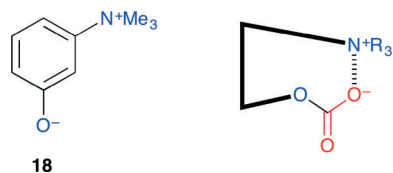
Fig. 14 Activation of CO_2 by ammonium betaine **18**.

Fig. 15 Immobilized NHC **19**.

Fig. 16 Dimeric Co(salen) complex **20**.
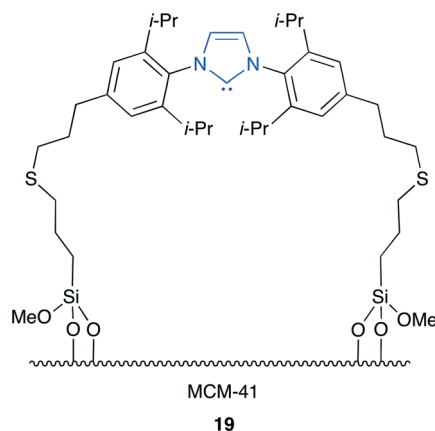
known that NHC can activate CO_2 by forming a stable imidazolium–carboxylate (NHC–CO_2) adduct. This is the efficient heterogeneous catalyst with high catalytic activity and reusability without metal and halogen. The *in situ* diffuse reflectance infrared fourier transform spectroscopy (DRIFTS) and thermogravimetric analysis (TGA) were used to investigate the reversible CO_2 capture–release behavior of **19**. **19** is an excellent CO_2 capture agent because it can form an NHC–CO_2 adduct at a relatively low temperature and can decarboxylate upon heating.

3. The synthesis of polycarbonates

Synthetic CO_2-based polymers with high CO_2 content are expected to find wide applications in green and sustainable society. Polycarbonates can be synthesized directly from CO_2 and epoxides (Scheme 4). Usually, mild reaction conditions are required to obtain uniformly distributed polycarbonates with high carbonate linkage. Under harsh reaction conditions, a polymer chain is shortened by the back-biting mechanism at the polymer terminus to give cyclic carbonate. Therefore, highly active catalysts are required for the copolymerization of epoxides and CO_2.

Nozaki and co-workers developed bimetallic catalyst **20**, which is a dimer of a Co(salen) complex (Fig. 16).[23] Epoxide
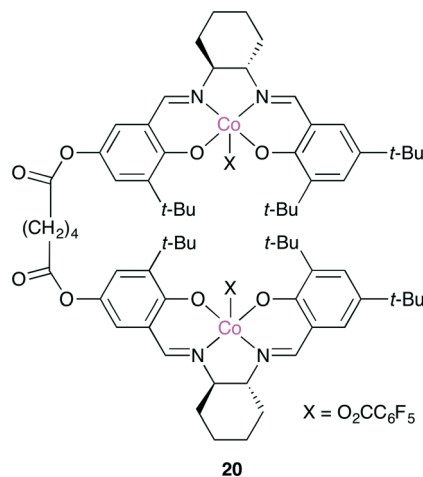
is activated by one metal center in **20**, whereas the alkoxide anion or carbonate anion of the polymer chain is coordinated to another metal center. These activated species might promote CO_2 insertion or nucleophilic attack to the epoxide, followed by the inter-nuclear migration. By repeating this process, polycarbonate is produced. Among several catalysts with various linker lengths, **20** was the most active probably because this bimetallic mechanism took place most efficiently.

Lu, Darensbourg and co-workers developed a highly active salen-type catalyst **21** bearing TBD (Fig. 17).[24] Although it is usually difficult to selectively copolymerize epoxide containing electron-withdrawing substituents, such as styrene oxide and epichlorohydrin, they succeeded in producing polycarbonate from epichlorohydrin with >99% polymer selectivity and >99% carbonate linkages by using **21** at 0 °C. Based on the mass spectra and X-ray crystal structures of reaction intermediates together with kinetic studies using *in situ* FT-IR spectroscopy, a catalytic cycle was also proposed for a binary catalyst system.

Niu and co-worker reported a new bifunctional Co(salen)-type catalyst with two Lewis basic units **22** (Fig. 18).[25] The copolymerization of CO_2 with propylene oxide selectively produced the alternating copolymer. In addition, the terpolymerization of CO_2, propylene oxide and cyclohexene oxide with a high cyclohexene carbonate content was also realized without the formation of cyclic carbonates or ether linkages. The glass
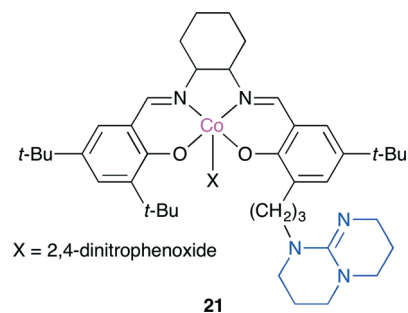

Scheme 4 The synthesis of polycarbonates from epoxides and CO_2.

Fig. 17 Bifunctional Co(salen) catalyst **21**.

Fig. 18 Bifunctional Co(salen) catalyst **22**.
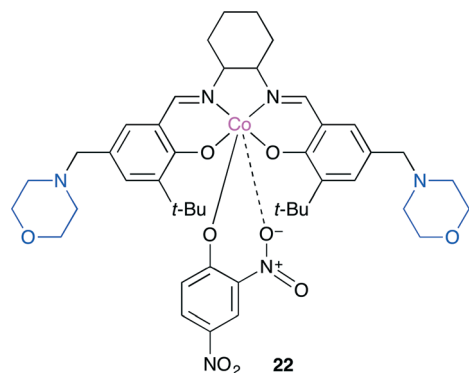

Fig. 20 Cr(salalen) catalyst **24**.

Fig. 21 Tetravalent metal complexes **25**.

transition temperature (T_g) of the terpolymer obtained was adjustable between 40 and 118 °C by controlling the relative ratios of propylene oxide and cyclohexene oxide.

Rieger and co-workers reported a bimetallic Cr(salphen) catalyst **23**, which has two salphen units bridged by a flexible alkyl chain (Fig. 19).[26] Although there are a few reports on dimeric salphen catalysts, they have a rigid bridging spacer with a long metal–metal distance. The copolymerization of propylene oxide and CO_2 with **23** was tolerant to dilution, giving a copolymer of a high molecular weight with a high selectivity, whereas the much slower copolymerization with a lower selectivity proceeded with the monomeric Cr(salphen).

The salalen-type catalyst **24** was developed by Nozaki and co-workers (Fig. 20).[27] Salalen is a reduced structure of salen, and the electronic and steric properties and flexibility of salalen are different from those of salen. **24** with [PPN]Cl ([PPN]$^+$ = bis(triphenylphosphoranylidene)iminium) as a co-catalyst showed a high catalytic performance for the copolymerization of cyclohexene oxide and CO_2 (TOF = 100 h^{-1}) at the atmospheric pressure of CO_2, which is the highest of the reported catalysts.

Furthermore, they reported a new catalyst **25** for the copolymerization of epoxides and CO_2 (Fig. 21).[28] Complexes **25** are composed of a tetravalent metal ion such as Ti, Zr, Ge
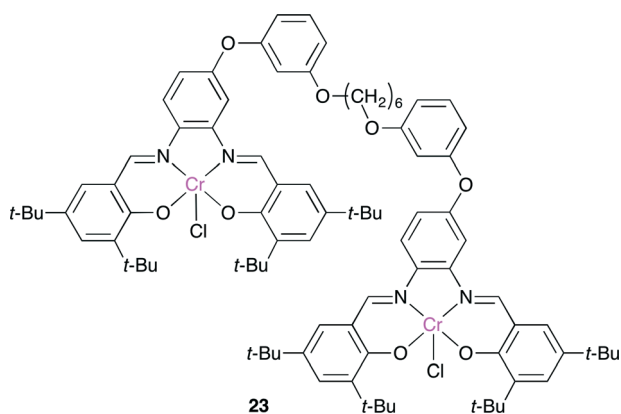
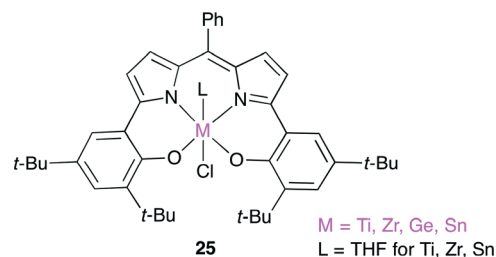and Sn, a trianionic [ONNO]-tetradentate ligand, and a monoanionic axial ligand. This is the first example of tetravalent metal complexes used as catalysts for the copolymerization. The Ti and Ge complexes were found to give the alternating copolymer with high carbonate linkage (TOF up to 76 h^{-1}). It is attractive to use the less toxic metals such as Ti and Ge, and further development is expected.

Coates and co-workers reported a method for the living multiblock copolymerization catalyzed by Zn(BDI) complex **26** (BDI = β-diiminate) (Fig. 22).[29] Various cyclohexene oxide derivatives containing protected alcohol, lipophilic, hydrophilic or fluorophilic functional groups could be copolymerized sequentially with CO_2 by **26** without any co-catalyst. Various block copolymers containing different carbonate units in a single chain were synthesized with good control of block sequence and length in one pot (Scheme 5).

4. Carboxylations with CO₂

In addition to the ring-opening reactions of epoxides with CO_2, much effort has been made to develop catalytic conversions of CO_2 into other useful compounds. In many cases,
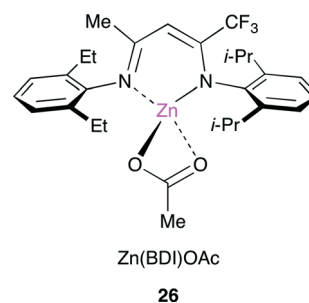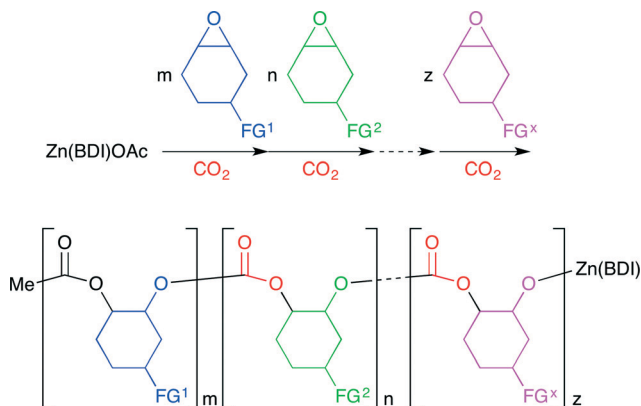

Fig. 19 Bimetallic Cr(salphen) catalyst **23**.

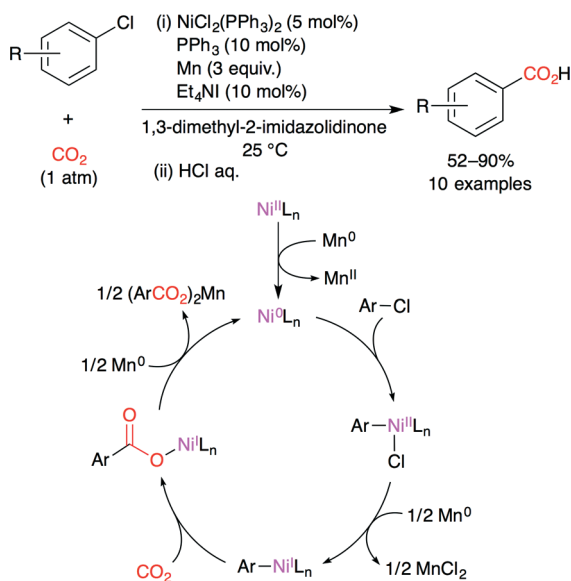

Fig. 22 Zn(BDI) complex **26**.

Scheme 5 The preparation of a multiblock cyclohexene carbonate copolymer.

researchers search for new reactions as well as new catalysts. In this section, catalytic carboxylation reactions with C–C bond formation are highlighted.

4.1 Carboxylation of aryl and benzyl halides

Tsuji and co-workers developed the nickel-catalyzed carboxylation of aryl and alkenyl chlorides with CO_2 (1 atm) at room temperature (Scheme 6).[30] This new catalytic system is also highly active for aryl bromides, tosylates and triflates. A proposed reaction mechanism is shown in Scheme 6. The Ni^{II} complex is reduced to a Ni^0 species upon treatment with Mn^0. The subsequent oxidative addition of aryl chloride gives a Ni^{II} intermediate. Ni^{II} is then reduced by the Mn^0/Et_4NI system to afford a Ni^I intermediate. This nucleophilic Ni^I species reacts with CO_2 to give the carboxylatonickel intermediate, which is reduced by Mn^0 to give the corresponding manganese carboxylate with the regeneration of the Ni^0 catalyst.

Martín and co-worker reported the Pd^0-catalyzed carboxylation of aryl bromides with CO_2 (Scheme 7).[31] The proposed reaction mechanism is shown in Scheme 7. The oxidative addition of aryl bromide to a Pd^0 complex forms a Pd^{II}–aryl species, and CO_2 insertion gives the Pd–carboxylate intermediate. Subsequent transmetalation with Et_2Zn delivers the Zn–carboxylate with the regeneration of the Pd^0 catalyst.
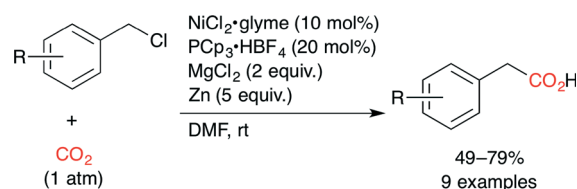
They also reported the Ni-catalyzed carboxylation of benzyl chlorides with CO_2 (Scheme 8).[32] A combination of $NiCl_2$·glyme, PCp_3·HBF_4 (Cp = cyclopentyl), $MgCl_2$ and Zn dust was found to provide phenylacetic acid derivatives in good yields at atmospheric CO_2 pressure at room temperature. Secondary and tertiary alkyl bromides also underwent the carboxylation under similar reaction conditions in moderate yields.

4.2 Hydrocarboxylation

Ohmiya, Sawamura and co-worker developed the reductive carboxylation of terminal alkenes by using a Cu(phen) complex (Scheme 9).[33] Reactive alkylborane is produced by the hydroboration of alkene with 9-borabicyclo[3.3.1]nonane (9-BBN), and
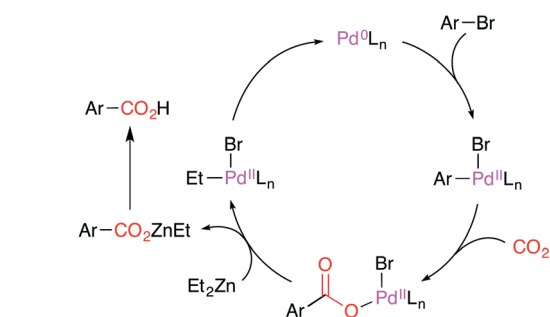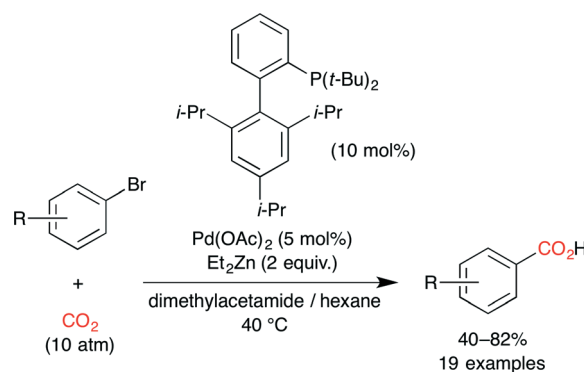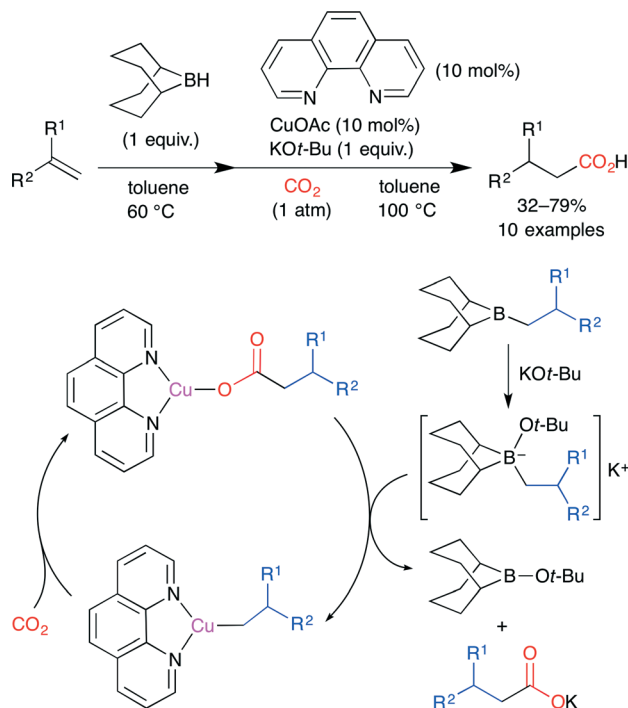

Scheme 7 The Pd-catalyzed carboxylation of aryl bromides with CO_2.

**Scheme 6** The Ni-catalyzed carboxylation of aryl chlorides with CO_2.

Scheme 8 The Ni-catalyzed carboxylation of benzyl chlorides with CO_2.

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Scheme 9 The Cu-catalyzed carboxylation of alkylboranes with CO_2.

Scheme 10 The Fe-catalyzed regioselective hydrocarboxylation of styrene derivatives with CO_2.

tetravalent borate is formed by the stoichiometric reaction of alkylborane with KO*t*-Bu. Subsequent B–Cu transmetalation between the Cu(phen) complex and alkylborate gives an alkylcopper(ı) species. Finally, CO_2 insertion takes place to afford the carboxylate copper complex. This is an attractive method because of easily accessible alkylborane and inexpensive Cu(phen).

Thomas and co-worker developed the Fe-catalyzed hydrocarboxylation of styrene derivatives by using a highly active bench-stable Fe^{II} precatalyst (Scheme 10).[34] Using 1 mol% $FeCl_2$, bis(imino)pyridine-based ligand (1 mol%), and EtMgBr (1.2 equiv.), a variety of styrene derivatives were transformed into the corresponding α-aryl carboxylic acids with high regioselectivity at atmospheric CO_2 pressure. The catalyst was found to be equally active with a loading of 0.1 mol%. The proposed mechanism is shown in Scheme 10. The alkylation of the iron precatalyst with EtMgBr and the coordination of styrene give an organometallic complex, which undergoes β-hydride elimination to give an iron hydride complex. The hydrometalation of styrene and the subsequent transmetalation with EtMgBr releases the hydromagnesiated intermediate with the regeneration of the initial complex. Finally, the hydromagnesiated intermediate reacts with CO_2 to form the carboxylated product.

## 4.3 Carboxylation *via* the C–H bond activation

In a transition metal-catalyzed carboxylation, an active carbon–metal bond is initially formed. In the presence of alkyl halide, however, a selective carboxylative coupling is difficult because the cross-coupling byproduct is easily formed from this active species and alkyl halide. Zhang, Lu and co-workers reported
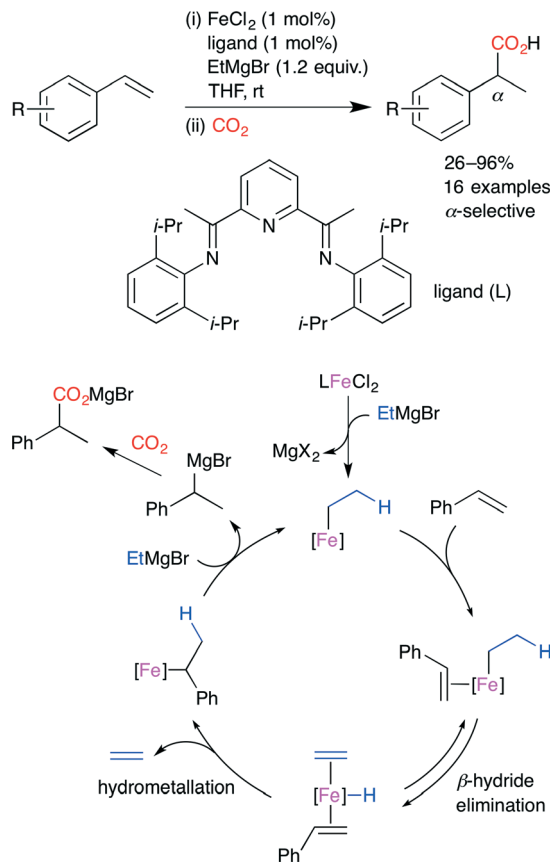
the carboxylative three-component coupling of terminal alkynes, allylic chlorides and CO_2 using an NHC–Cu^I complex (Scheme 11).[35] In this particular case, the use of less reactive allylic chloride suppressed the cross-coupling side reaction, leading to a high selectivity. Carboxylic acid esters were obtained directly from the reaction mixture. The catalyst could be easily recovered in a high yield by chromatographic separation.

Iwasawa and co-workers succeeded in the development of Rh^I-catalyzed direct carboxylation of aromatic compounds *via* chelation-assisted C–H bond activation (Scheme 12).[36] It is well known that Rh^I complexes are efficient catalysts for C–H activation and that an arylrhodium(ı) species has sufficient nucleophilicity. A proposed catalytic cycle is shown in
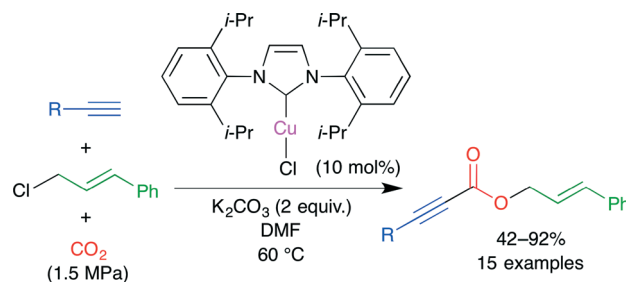
Scheme 11 The Cu-catalyzed carboxylative coupling of terminal alkynes, allylic chlorides and CO_2.
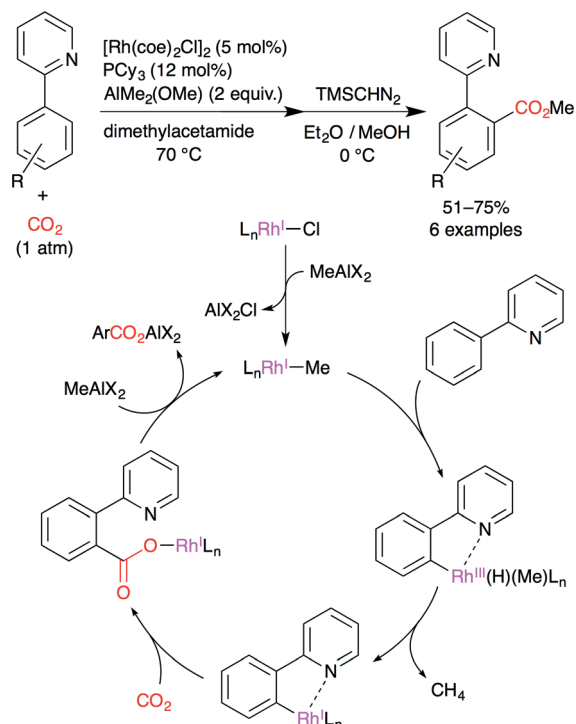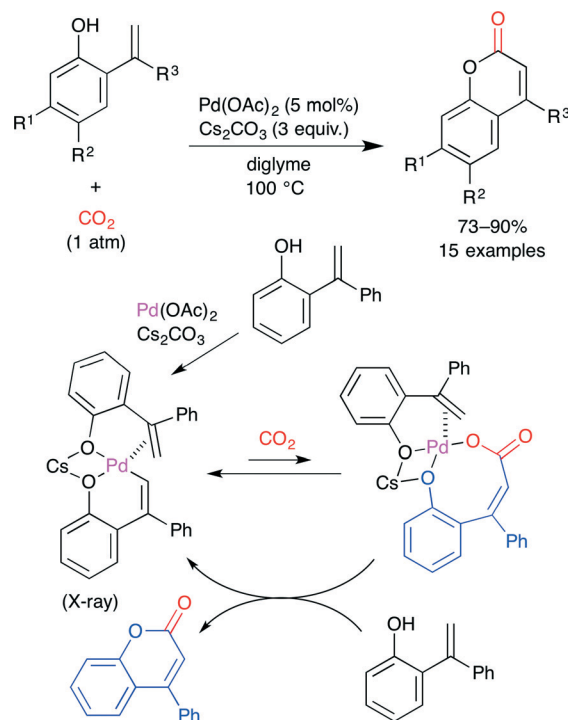
Scheme 12 The Rh-catalyzed direct carboxylation of arenes with CO_2.

Scheme 13 The Pd-catalyzed direct carboxylation of 2-hydroxystyrene derivatives with CO_2.

Scheme 12. (i) A methylrhodium(I) species is generated by the reaction of Rh^I chloride with the methylaluminum reagent. (ii) C–H bond activation occurs at the *o*-position by the chelation effect of the pyridyl group. (iii) The reductive elimination of methane gives the arylrhodium(I) species. (iv) The nucleophilic carboxylation of arylrhodium(I) affords the rhodium carboxylate. (v) Transmetalation with the methyl-aluminum reagent gives the aluminum carboxylate, regenerating the initial methylrhodium(I) species. The pyrazole ring can also be used as a directing group.

This group also reported the Pd^{II}-catalyzed direct carboxylation of the alkenyl C–H bond with CO_2 (Scheme 13).[37] The treatment of 2-hydroxystyrenes with $Pd(OAc)_2$ and Cs_2CO_3 under atmospheric CO_2 pressure produced coumarins in good yields. The reaction mechanism, which was proposed on the basis of the X-ray crystal structure and reactivity test of the intermediates, is shown in Scheme 13. First, the six-membered alkenyl palladium intermediate is generated by the chelation-assisted alkenyl C–H bond cleavage of 2-hydroxystyrene with $Pd(OAc)_2$ along with the coordination of the second mole-cule of 2-hydroxystyrene. Subsequently, this alkenyl palladium species undergoes reversible carboxylation to afford a palladium carboxylate intermediate. This is replaced by another molecule of 2-hydroxystyrene to release the product with the regeneration of the six-membered alkenyl palladium intermediate.

The carboxylation of a $C(sp^3)$–H bond with CO_2 is one of the most challenging transformations in current organic chemistry. A novel sequential protocol for the benzylic $C(sp^3)$–H carboxylation *via* $C(sp^3)$–H silylation catalyzed by Ir^I or Ru^0 complexes was developed by Mita, Sato and co-workers (Scheme 14).[38]
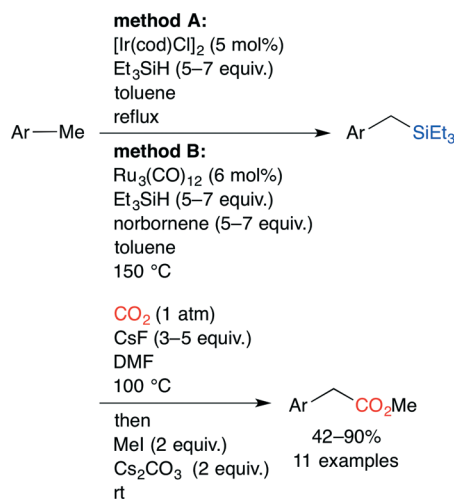
Scheme 14 Benzylic $C(sp^3)$–H carboxylations.

Because the pyridyl group in the substrate behaves as a directing group, Ir and Ru complexes can form stable 5–7 membered complexes when the benzylic $C(sp^3)$–H bond is selectively activated by these chelation modes (Fig. 23).

4.4 Other carboxylations

Feng, Bao and co-workers synthesized the Pd^{II} complex with the air-stable *P,N*-bidentate ligand (Fig. 24), where the cyclic secondary amine moiety is linked to the benzene ring of triphenylphosphine.[39] The X-ray crystal structure indicated that the soft P and hard N atoms in the ligand are coordinated
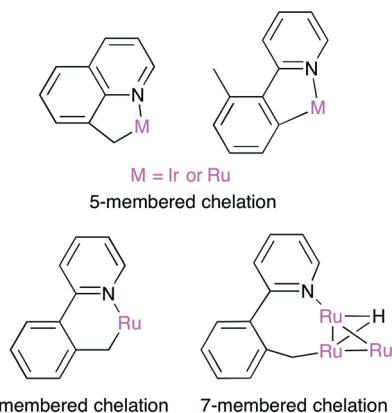
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Fig. 23 The chelation mode between benzylic C(sp³)–H and Ir or Ru.
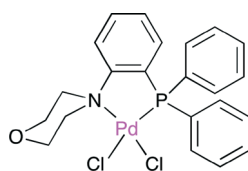
Fig. 24 The Pd complex with the *P,N*-bidentate ligand.

Scheme 16 The carboxylation of allylstannanes and allylboranes with CO_2.

Scheme 17 The carboxylative cyclization of propargylic alcohol and CO_2.
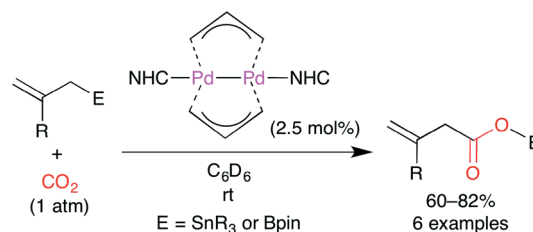
to the Pd^{II} center. The selective synthesis of δ-lactone was effected by the palladium-catalyzed telomerization of 1,3-butadiene with CO_2 (Scheme 15). Among several ligands prepared, this *P,N*-bidentate ligand (Fig. 24) was the most suitable for this synthesis.

Hazari and co-workers developed a facile synthesis of a Pd^I-bridging allyl dimer and its use in the catalytic carboxylation of allylstannanes and allylboranes with CO_2 (Scheme 16).[40] The allyl-bridged Pd^I dimer is attractive because of a metal–metal bond, two bridging allyl ligands, and a terminal ligand (NHC). This catalyst had been derived from (η¹-allyl)(η³-allyl)Pd(L) complex, which is air-, moisture-, and temperature-sensitive. The authors found a more efficient synthetic method, which is a direct reaction of Pd(allyl)$_2$ with NHCs. Bridging allyl ligands are nucleophilic like η¹-allyl ligands rather than electrophilic like η³-allyl ligands. The insertion of CO_2 followed by trans-metallation gives the product.
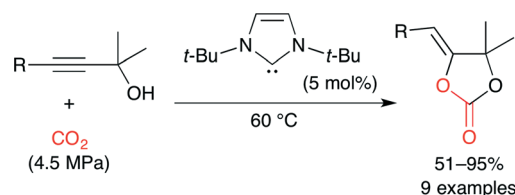
Ikariya and co-workers reported that NHCs and the corresponding CO_2 adducts act as effective catalysts for carbonate synthesis under relatively mild reaction conditions (Scheme 17).[41] NHCs are expected to exhibit similar chemical properties to

tributylphosphine (Bu$_3$P) which forms zwitterionic CO_2 adducts (Fig. 25) to promote the nucleophilic addition of CO_2 to electrophiles. This method can easily synthesize hindered internal cyclic carbonates.

They have also demonstrated the Pd-catalyzed carboxylative cyclization of α-allenyl amines to give oxazolidinones (Scheme 18).[42] A possible catalytic mechanism is as follows. (i) The oxidative addition of carbamic acid generated gives a hydridopalladium species. (ii) The allene moiety then inserts into the Pd–H bond to give an η³-allylpalladium intermediate. (iii) The reductive elimination gives the cyclization product. This is the first example of the Pd-catalyzed cyclic urethane synthesis *via* the intramolecular addition of carbamic acid. This direct addition system is an environmentally benign process giving no wastes.

Bhanage and co-workers used polymer-supported diol-functionalized ionic liquids as a catalyst for the coupling of aziridine and CO_2 (Scheme 19).[43] Hydrogen bonding between the aziridine and the vicinal hydroxy groups in the ionic liquid activates the aziridine ring. The Br⁻ anion selectively attacks the α-position of the phenyl group to ring-open. The CO_2 insertion followed by cyclization affords the product. The catalyst was readily recovered by simple filtration, and the catalytic activity was retained after four-time reuse.

The benzoxazin-2-one and 4-hydroxyquinolin-2(1*H*)-one skeletons are seen in several drugs. Ag-catalyzed incorporation of CO_2 into *o*-alkynylanilines was developed by Yamada and co-workers. By using AgNO$_3$ and 1,8-diazabicyclo[5.4.0]undec-7-ene
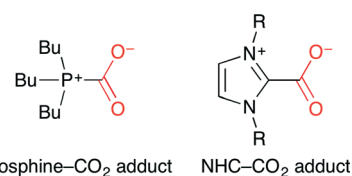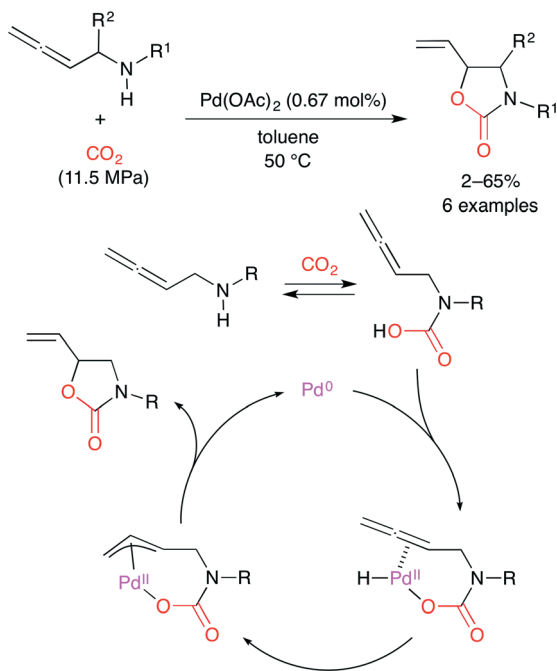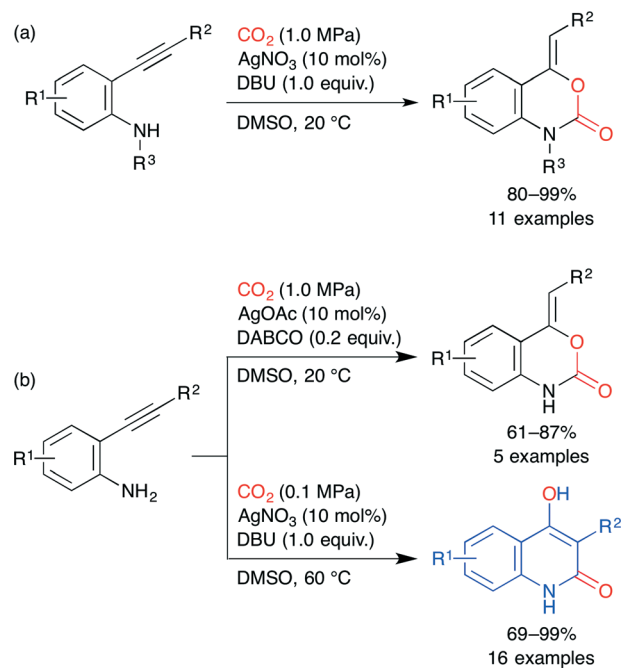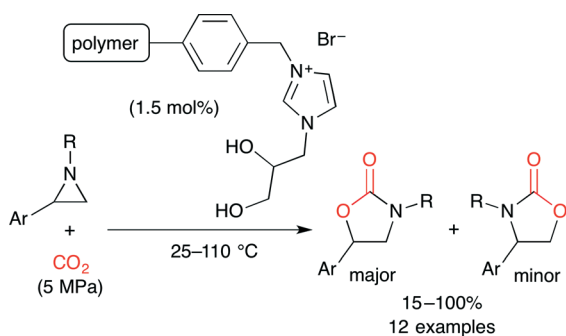

Scheme 15 The Pd-catalyzed telomerization of 1,3-butadiene with CO_2.
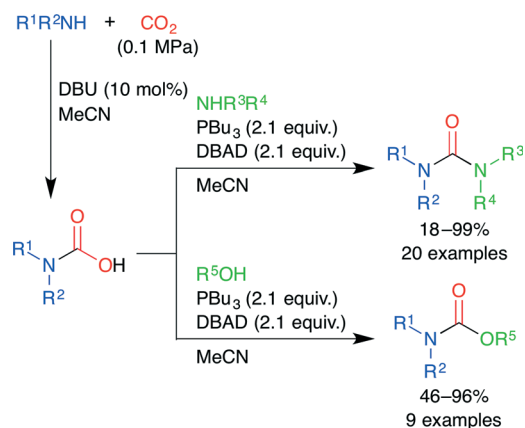

Fig. 25 Zwitterions of phosphine–CO_2 and NHC–CO_2 adducts.

Scheme 18 The carboxylative cyclization of allenic amines.

Scheme 19 The carboxylation of aziridine with CO_2.

Scheme 20 The Ag-catalyzed incorporation of CO_2 into o-alkynylanilines.

Scheme 21 The synthesis of ureas and carbamates via carbamic acids generated by the DBU-catalyzed reactions of amines and CO_2.

(DBU) under CO_2, secondary o-alkynylanilines were converted into the corresponding benzoxazin-2-ones (Scheme 20a).[44] Primary o-alkynylanilines also underwent the same reaction by using 1,4-diazabicyclo[2.2.2]octane (DABCO) instead of DBU. Surprisingly, when DBU was used for primary o-alkynylanilines, 4-hydroxyquinolin-2(1H)-ones were produced in excellent yields (Scheme 20b).[45] An intramolecular rearrangement involving the generation of isocyanate from benzoxazin-2-one formed in situ is proposed. In both cases, the Ag[I] ion activates the C–C triple bond most efficiently to promote the cyclization of a carbamate intermediate.

A mild and efficient synthesis of ureas and carbamates via carbamic acids generated by the DBU-catalyzed reaction of amines and CO_2 was developed by Peterson and co-workers (Scheme 21).[46] The carbamic acids generated from primary amines were dehydrated under Mitsunobu conditions to give isocyanates, which reacted with amines and alcohols to yield the corresponding ureas and carbamates, respectively. On the other hand, the carbamic acids from secondary amines react with activated alcohols by the S_N2 mechanism. Various unsymmetrical di- and trisubstituted ureas and carbamates could be easily constructed. This parallel process may be useful for the synthesis of various building blocks containing urea or carbamate.

5. The reduction of CO_2

The reduction of CO_2 can produce carbon monoxide (CO), formic acid, methanol, methane, and so on. Recently, catalytic reductions of CO_2 have been studied actively. For example, Zhang and co-worker achieved the NHC-catalyzed reduction of CO_2 to CO using aromatic aldehydes as reductants (Scheme 22).[47] Originally, they had expected that carbonate and/or anhydride would be obtained from the reaction between cinnamaldehyde

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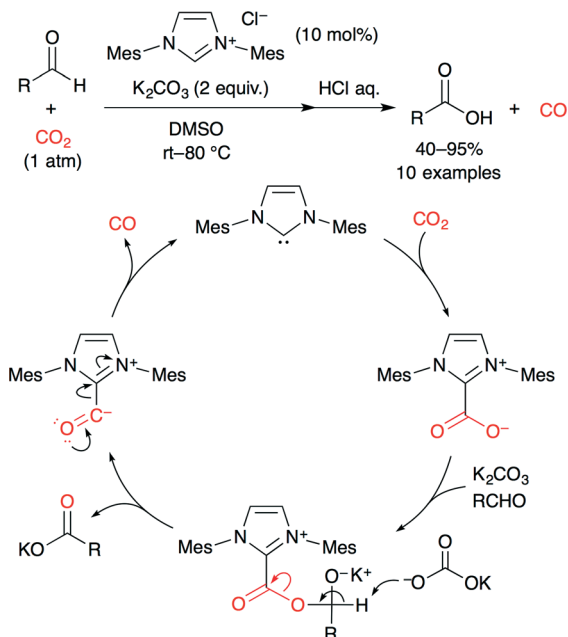
Scheme 22 The NHC-catalyzed reduction of CO_2.

and imidazolium–carboxylate (NHC–CO_2), but actually, CO_2 behaved as an oxidant. A catalytic cycle is shown in Scheme 22. (i) NHC reacts with CO_2 to form NHC–CO_2. (ii) The carboxylate attacks the formyl group, generating a possible intermediate. (iii) Deprotonation results in the NHC–CO complex and a carboxylate salt *via* the C–O bond splitting. (iv) The NHC–CO complex releases CO with the regeneration of the NHC.

The catalytic hydrogenation of CO_2 to formate was reported by Nozaki and co-workers (Scheme 23).[48] By using a PNP-ligated Ir^{III} trihydride complex, potassium formate was formed from CO_2 in aqueous potassium hydroxide with an extremely high TON (3 500 000) at 120 °C and TOF (150 000 h^{-1}) at 200 °C. A plausible mechanism is shown in Scheme 23. (i) CO_2 is inserted into the Ir^{III} trihydride complex. (ii) Deprotonative
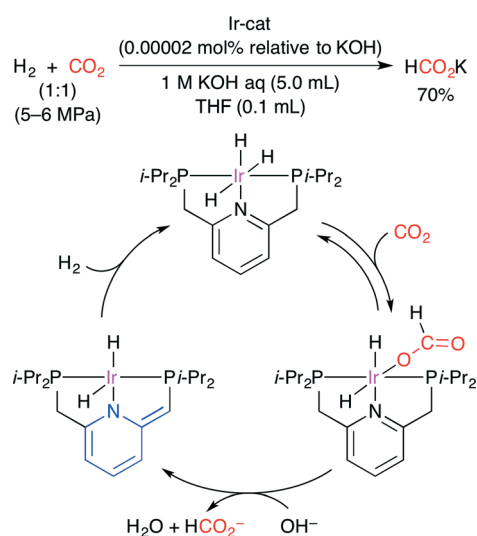
dearomatization promotes the dissociation of the formate ligand. (iii) Hydrogenation regenerates the initial trihydride complex.

The catalytic hydrogenation of CO_2 was further studied by Hazari and co-workers.[49] Computational calculations on several Ir complexes indicated that CO_2 insertion is *trans*-influenced and that hydride is the best *trans*-influence ligand. In addition, they found a promising Ir^{III} trihydride complex exhibiting a deviation from prediction (Scheme 24a). It has a hydrogen-bond donor in the secondary coordination sphere, and CO_2 insertion seems to be favored by hydrogen bonding, which was indeed supported by DFT calculations. The transition-state stabilization by hydrogen bonding was calculated to be −4.59 kcal mol^{-1}. The CO_2-inserted Ir^{III} complex in Scheme 24a was characterized by NMR, IR and X-ray diffraction analysis. This CO_2-inserted Ir^{III} complex, which is air-stable and water-soluble, produced potassium formate from CO_2 and H_2 in aqueous KOH at 185 °C in up to 70% yield with a high TON of 348 000 (Scheme 24b).

The catalytic conversion of CO_2 into methane using a frustrated Lewis pair (FLP) was developed by Piers and co-workers (Scheme 25).[50] A FLP consists of a bulky Lewis acid and a bulky Lewis base which cannot be quenched by each other because of steric hindrance. As shown in Scheme 25, the ammonium hydridoborate ion pair $[TMPH]^+[HB(C_6F_5)_3]^-$, which was prepared by the treatment of a FLP (TMP/B($C_6F_5)_3$) with H_2, reacted with CO_2 to give a formatoborate. The subsequent silylation of formatoborate with Et_3SiH and B($C_6F_5)_3$ afforded formatosilane, which was ultimately reduced to methane by further hydrosilylation.

Zhang, Ying and co-worker developed the NHC-catalyzed reduction of CO_2 to methanol (Scheme 26).[51] It is known that NHCs behave as nucleophiles for CO_2 to form imidazolium carboxylates (NHC–CO_2 adducts). The reaction is proposed to proceed in the following way. The carboxylate moiety of the NHC–CO_2 adduct attacks the silane center, and simultaneous hydride transfer forms formoxysilane. The formoxysilane reacts with free hydrosilanes in the presence of NHC. Methanol is produced by further reduction and workup. NHC could be reduced to 0.05 mol%, and the TON reached 1840. This is the first example of hydrosilylation of CO_2 using an organocatalyst.

Scheme 23 The Ir-catalyzed hydrogenation of CO_2.
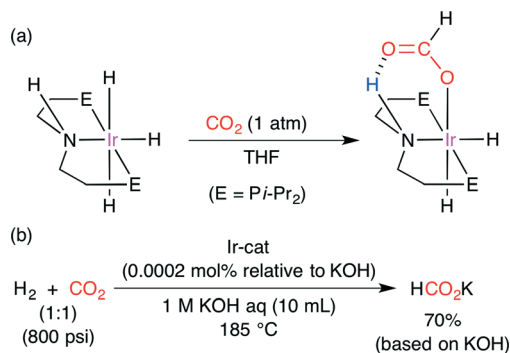
Scheme 24 (a) The insertion of CO_2 into the Ir-trihydride complex. (b) The Ir-catalyzed hydrogenation of CO_2.
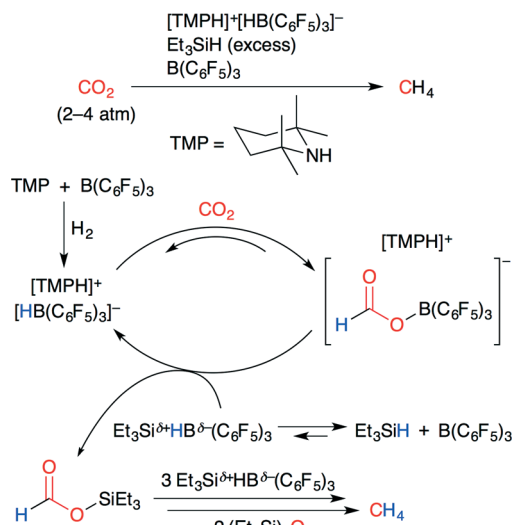
Scheme 25 The FLP-catalyzed deoxygenative hydrosilylation of CO_2.

Cantat and co-workers reported organocatalytic reductive formylation of amines with CO_2 (Scheme 27).[52] The three-component reaction of CO_2, amine and $PhSiH_3$ in the presence of TBD (5 mol%) afforded formamide. As a result of the screening of base catalysts, TBD showed the best performance, which is due to the formation of the carbamate salt (Fig. 26). The hydride transfer from silicon to carbon is facilitated by the hydrogen bonds between the carbamate anion and the TBDH$^+$ cation. Secondary amines were more reactive than primary amines, and aliphatic amines were more reactive than aromatic amines, which indicates that the activity was mainly governed by the basicity of the amines.
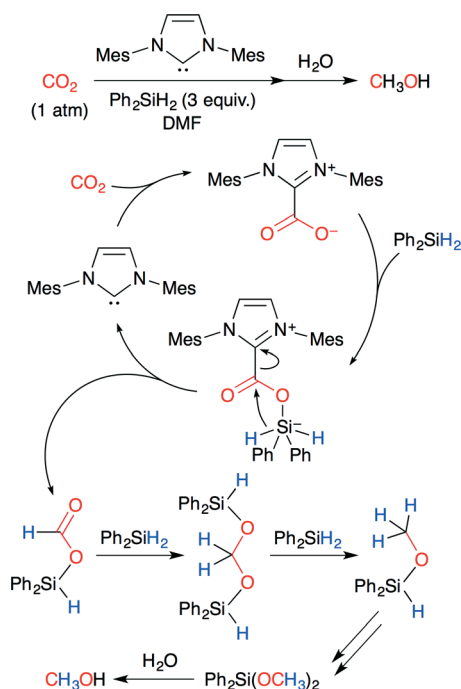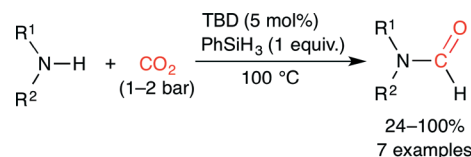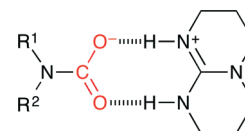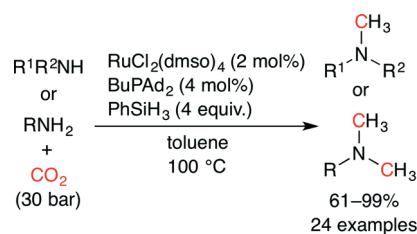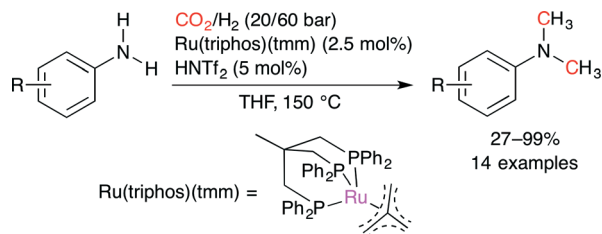

Scheme 26 The NHC-catalyzed hydrosilylation of CO_2.

Scheme 27 The TBD-catalyzed reductive formylation of amines with CO_2.

Fig. 26 The formation of the carbamate salt with TBD.

Cantat and co-workers found that Zn^{II} salts are effective for promoting the reactions of amines with CO_2 and hydrosilanes to give N-methylamines. They screened many combinations of Zn^{II} salts and neutral ligands and found that $IPrZnCl_2$ was the best catalyst (Scheme 28).[53] $PhSiH_3$ and THF were the best hydride source and solvent, respectively. Various primary and secondary amines were methylated. They proposed a possible reaction pathway. The Zn-catalyzed reductive formylation of amine with CO_2 and $PhSiH_3$ would give formamide, which would be further reduced to N-methylamine by the Zn-catalyzed hydrosilylation.

Beller and co-workers independently reported the methylation of amines with CO_2 using a Ru catalyst (Scheme 29).[54] As a result of the screening of 15 metal precursors including Ru, Rh, Cu and Fe complexes and 12 phosphine and nitrogen ligands, a combination of $RuCl_2(dmso)_4$ and $BuPAd_2$ showed the highest catalytic performance. A variety of aromatic and aliphatic, secondary and primary amines were successfully transformed into the desired tertiary amines in good to excellent yields. Notably, functional groups such as ester and nitrile were tolerated under the reaction conditions.
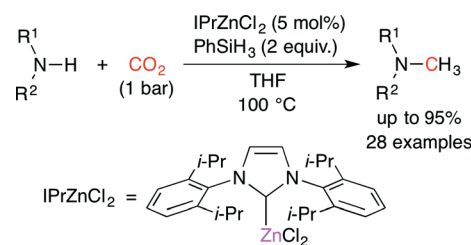
Scheme 28 The Zn-catalyzed methylation of amines with CO_2.

Scheme 29 The Ru-catalyzed methylation of amines with CO_2.

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Scheme 30 The Ru-catalyzed methylation of aromatic amines using CO_2 and H_2.
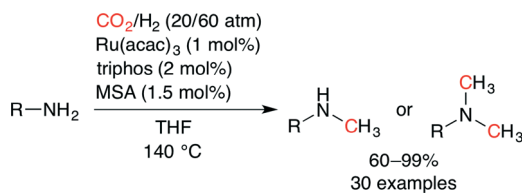
Scheme 31 A general catalytic methylation of amines.

Klankermayer and co-workers disclosed the Ru-catalyzed methylation of primary and secondary aromatic amines with CO_2 and H_2 (Scheme 30).[55] A combination of the triphos-based Ru complex, Ru(triphos)(tmm), with an acid such as trifluoromethanesulfonylimide (HNTf$_2$), methanesulfonic acid (MSA), and p-toluenesulfonic acid (p-TsOH) afforded methylated products in excellent yields. The acid co-catalyst was essential for the reaction.

Beller and co-workers also independently succeeded in the Ru-catalyzed methylation of aromatic and aliphatic amines with CO_2 and H_2 (Scheme 31).[56] By using a ruthenium(III) precursor and triphos, the desired methylated amines were obtained in good to excellent yields. Furthermore, selective mono-methylation of primary amines was achieved by tuning the reaction time and catalyst loading. Although aliphatic amines showed a poor reactivity under the standard conditions, the replacement of MSA with LiCl (7.5 mol%) gave satisfactory results. Several control experiments indicated that methylation of amines proceeded predominantly via formamide intermediates.

6. Conclusions and outlook

The efficient conversion of CO_2 into useful compounds is a longstanding dream of synthetic chemists. Catalysts play a key role in expanding the synthetic potential. Indeed, new reactions and new catalysts have been actively developed over the past several years. In this perspective, we provide an overview of the recent progress. Although the efficiency of CO_2 fixation is far below that of enzymatic reactions in photosynthesis, synthetic methods are rich in variation. The coupling reactions of CO_2 with epoxides to give cyclic carbonates or polycarbonates are highly atom-efficient, producing no by-products. Some of the catalysts recently developed showed extremely high TON and TOF or a high reusability without the loss of catalytic activity. Catalytic carboxylation reactions involving C–C bond formation are very useful and powerful,

and synthetic variation is increasing. Not only C–X bonds but also C–H bonds can be activated by transition metals. The number of new methods for the reduction of CO_2 is also increasing rapidly. CO_2 can be successfully reduced into CO, formic acid, methanol, methane, formamide, or methylamine using hydrosilane or H_2 as a reductant. Organocatalysts as well as metal catalysts are effective for these transformations. The electrochemical or photochemical reduction of CO_2 has also been studied, although they are out of range of this perspective.[57] Further developments and breakthroughs toward the creation of a green and sustainable society are expected.

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